

Simulations of Self-Assembly in Surfactant and Nanoparticle Systems

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This lecture focuses on self-assembly of ionic surfactant into micelles, and on structure and dynamics for solvent-free grafted nanoparticles. The importance of electrostatic interactions on self-assembly of surfactants and biological systems has been widely acknowledged. Most theoretical approaches for these systems are based on mean-field approximations that neglect higher order correlations that are particularly important for multivalent ions and in environments of low dielectric permittivity. We have developed implicit-solvent ionic surfactant models and have used them in Grand Canonical Monte Carlo simulations to investigate the critical micelle concentration, aggregation number and micellar shape in the presence of explicit salt. Explicit-solvent models have also been studied, using GPU computing to reach the microsecond time scales necessary for equilibration. We present evidence that the free surfactant concentration is much lower than the cmc for strongly micellizing systems at the relatively high concentrations accessible by simulations. Thus, one must account for counterion association and extrapolate with respect to overall surfactant concentration when determining the CMC from the raw simulation data. Finally, we use molecular dynamics simulations over microsecond time scales to study the structure and dynamics of coarse-grained models for nanoparticle-based ionic liquids. Even though electrostatic interactions between oppositely charged ions at contact are much greater than the thermal energy, we find that chain dynamics at intermediate time scales are dominated by chain hopping between core particles.